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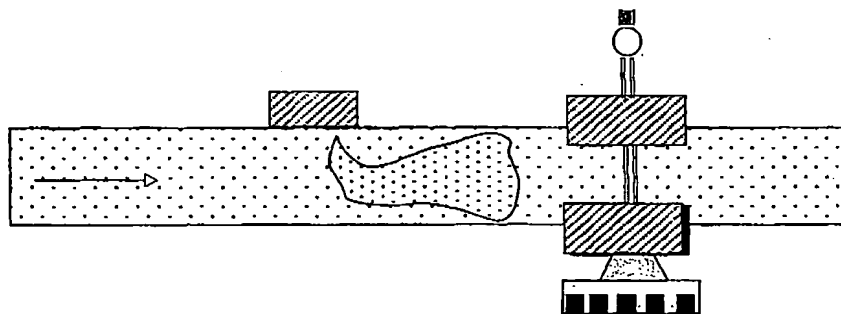
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(54) Title: APPARATUS AND METHOD FOR ANALYSING DOWNHOLE WATER CHEMISTRY



(57) Abstract: The invention concerns an apparatus for analysing water chemistry. According to the invention, the apparatus is adapted to operate downhole and comprises a colouring agent supply device for supplying a colouring agent to a water sample, the colour of the water sample thus supplied being indicative of the water sample chemistry, and a colorimetric analyser arranged to determine the colour of the water sample.

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For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

APPARATUS AND METHOD FOR ANALYSING DOWNHOLE WATER CHEMISTRYField of the Invention

The present invention relates to an apparatus and method for downhole water chemistry analysis.

5 Background of the Invention

Well operators commonly need to understand downhole water chemistry to help them decide production strategies and determine corrosion rates, scale formation rates, formation geochemistry etc.

10 More specifically, the pH and qualitative/quantitative analysis of the presence of specific ions in downhole water are often required.

Conventionally, water chemistry measurements are performed in the laboratory on fluid samples retrieved from below ground.

15 However, water chemistry is not often preservable over the temperature and pressure changes typically induced by transportation from subterranean locations to the surface, and so a chemistry measurement of a sample collected for laboratory analysis will not always provide a result that can
20 be related to the downhole value. Consequently, the water chemistry measured in the laboratory may vary significantly from that existing downhole.

Summary of the Invention

25 An object of the present invention is to provide a more reliable analysis of downhole water chemistry.

Accordingly, in a first aspect, the present invention provides an apparatus for analysing water chemistry, the apparatus being adapted to operate downhole and comprising:

a colouring agent supply device for supplying a colouring agent to a water sample, the colour of the water sample thus supplied being indicative of the water sample chemistry, and

a colorimetric analyser arranged to determine the colour of the water sample.

An advantage of the apparatus is that it allows *in situ* analysis to be performed, thereby avoiding the problems associated with transporting water samples to the surface.

The present invention is at least partly based on the realisation that colorimetric analysis is a technique that can be adapted for performance downhole, i.e. in relatively demanding and hostile conditions.

In one embodiment the apparatus is installed downhole (e.g. in a hydrocarbon well or an aquifer).

Preferably the colorimetric analyser is connected to a processor for determining the water sample chemistry from the colour of the water sample. The processor may also be adapted for use downhole, or alternatively it may be intended for remote installation e.g. at the surface. For example the processor may be a suitably programmed computer.

The water sample colour may be indicative of e.g. water pH or a selected ion concentration level.

In one embodiment the colorimetric analyser comprises a spectrometer. An advantage of a spectrometer-based approach to colour analysis is that it has the potential to provide fast answers to questions of pH, corrosion chemistry and scale formation, which can be crucial for deciding e.g. completion design and materials and scale treatment programs.

A further aspect of the present invention provides for the use of the apparatus of the previous aspect for *in situ* analysis of downhole water chemistry.

In another aspect the present invention provides a method for analysing downhole water chemistry, the method comprising the steps of:

(a) supplying a colouring agent to a downhole water sample, the colour of the water sample thus supplied being indicative of the water sample chemistry, and

(b) determining the colour of the water sample, wherein steps (a) and (b) are performed *in situ*.

In another aspect the present invention provides a method for monitoring contamination of downhole water, the method comprising the steps of:

(a) adding a tracer agent to a fluid which is a potential contaminant of the downhole water,

(b) supplying a colouring agent to a sample of the downhole water, the colour of the water sample thus supplied being indicative of the presence of the tracer agent, and

(c) determining the colour of the water sample, wherein steps (b) and (c) are performed *in situ*.

The potential contaminant may be drilling mud filtrate. The downhole water may be either connate or injected water.

Brief Description of the Drawings

Specific embodiments of the present invention will now be described with reference to the following drawings in which:

Figure 1 shows a schematic diagram of a Live Fluid Analyser installed on a flow line,

Figure 2a shows the room temperature absorbance spectra of (a) the acid form of phenol red, (b) the base form of phenol red, (c) phenol red in a pH 8 solution, and (d) a weighted sum of the acid and base form spectra fitted to the pH 8 solution absorbance spectrum,

Figure 2b shows graphs of base fraction of phenol red (right hand vertical axis) and calculated pH (left hand vertical axis) as functions of prepared solution pH,

Figure 3a shows the room temperature absorbance spectra obtained from (a) phenol red in deionised water and (b) phenol red in deionised water after heat treatment at 150°C for 24 hours, and

Figure 3b shows the absorbance spectra obtained from (a) phenol red in a pH 7.4 buffer solution at 22°C and (b) phenol red in the pH 7.4 buffer solution at 150°C.

Detailed Description of the Invention

In general terms, the present invention relates to downhole colorimetric analysis. A preferred approach for the determination of pH and detection of the presence of specific ions involves injecting a specific indicator or reagent into a sample of water and determining the resulting colour of the fluid with an optical spectrometer.

Ions of interest for detection include those of Ca, Ba, Sr, Al, Cl, F, Fe, Mg, K, Si, Na, and ions containing sulphur and carbon (for example carbonate, bicarbonate, sulphate). Use of colorimetric and spectrometric analysis along with procedures and reagents required to determine the presence/quantity of some of these ions have been described in the literature (Vogel, A. I., *Text-Book of Quantitative Inorganic Analysis*,

3rd Edition, Chapter 10, John Wiley, 1961; Sandell E. B., *Colorimetric Determination of Traces of Metals*, 3rd Edition, Interscience Publishers, 1959). However, we propose, for the first time, the application of these methods, in a downhole environment, to the analysis of downhole water as found in oil and gas fields, as well as aquifers. Typical temperatures and pressures found in a downhole environment are in the range of 125°C and 10,000 psi, respectively; however they can go up to as high as 175°C and 20,000 psi.

10 To perform quantitative measurements of pH or ion concentration, the optical absorption of the unknown species can be determined either relative to a standard solution (which could be the water sample itself prior to indicator/reagent addition) or with a stable and previously
15 calibrated spectrometer.

Desirably, the spectrometer should be capable of operating over the visible spectrum of 400 to 760 nm, which is from ultraviolet to infrared respectively.

In one embodiment we propose fitting a known Modular Dynamic Tester (MDT) with a Live Fluid Analyzer (LFA) module (R.J. Andrews et al., *Oilfield Review*, 13(3), 24-43). The LFA would inject coloured indicators to the water flowing through the MDT so that pH can be determined. It can also add suitable reagents to the water for determination of the
25 presence/concentration of selected ions.

Figure 1 shows a schematic diagram of the LFA installed on a flow line 1, the other parts of the MDT not being shown. An arrow indicates the direction of water flow in the flow line. The LFA has an upstream dye injector 6 and a downstream
30 optical analyser 2. The analyser comprises a light source 3 on one side of the flow line and a facing light detector 4 on

the opposite side of the flow line. When a preselected indicator or reagent 5 is injected into flow line it mixes with the water and is carried downstream to the analyser, whereupon the detector generates a signal indicative of the colour of the water. If required a mixer, not shown in the figure, such as a double helix, can be used to promote mixing of the water and dye. A processor (not shown) then determines the water chemistry from the signal e.g. using approaches discussed below.

- 10 Such colorimetric analysis also allows contamination of formation water by water-based mud filtrate to be detected. This can be achieved by suitable indicator/reagent selection such that the water-based mud filtrate and formation water generate different respective colours.
- 15 Another option is to add a tracer ion or other species (for example, nitrate, iodide or thiocyanate ions) to the drilling fluid. A reagent can then be used in the LFA, which produces a colour change in the presence of the tracer so that the tracer can be detected and preferably quantified. In this way
- 20 real-time monitoring of connate water for contamination by the filtrate can be achieved.

A possible reagent for detecting iodide is the iodobismuthite ion, formable from a solution of bismuth in dilute sulphuric acid. This ion gives a yellow orange colouration and is

25 sensitive up to 1% iodide (Vogel, A. I., *Text-Book of Quantitative Inorganic Analysis*, 3rd Edition, Chapter 10, p803 John Wiley, 1961).

We now describe how indicator colouration can be used to measure pH. However, similar considerations apply when the

30 colour of any reagent is being used to measure ion concentration.

For pH measurements the choice of indicator depends to a significant extent on the accuracy with which the pH is required. As an example, we take a universal indicator, a volume of which has been injected into the sample flowline upstream of the optical detector. The indicator volume is determined by the flow rate of the water and intensity of the colour and is usually a small fraction of the total volume. The universal indicator may be formed e.g. from a mixture of 0.2 g of phenolphthalein, 0.4 g methylred, 0.6 g dimethylazobenzene, 0.8 g bromothymol blue, and 1 g of thymol blue in 1 l ethanol. To this solution is added NaOH(aq) until the solution appears yellow. The colours of the solution as a function of pH are listed in the table below (Vogel, A. I., *Text-Book of Quantitative Inorganic Analysis*, 3rd Edition, Chapter 1.30, p59 John Wiley, 1961).

pH	2	4	6	8	10	12
Colour	Red	Orange	Yellow	Green	Blue	Purple

An alternative is to use a plurality of indicators each of which is specific to a respective pH range. This may result in a more precise determination of pH.

The pH of an unknown solution may be obtained using the equation below (R.G. Bates, *Determination of pH: Theory and Practice*, Chapter 6, John Wiley, 1964):

$$pH = pK_a + \log \frac{\gamma_B}{\gamma_A} + \log \frac{B}{A} \quad (1)$$

where K_a is the thermodynamic equilibrium constant for the indicator and is a function of temperature; A and B are the respective fractions of the acid and base forms of the indicator; and γ_A and γ_B are respective activity coefficients of the acid and base forms of the indicator, and depend on ionic

strength of the solution and temperature. Both K_a and activity coefficients could be weak functions of pressure as well.

The fraction of the indicator that exists in the acid form (A) and base form (B) may be measured spectroscopically. The absolute concentration of the dye does not appear in the equation and hence the pH calculation is independent of the volume of dye injected or the flow rate of the water stream as long as the concentration is such that Beer's law is satisfied. The functional dependence of K_a on temperature (T) has been studied and measured for a number of reactions and a general equation that can describe this dependence is (D. Langmuir, *Aqueous Environmental Geochemistry*, Chapter 1, Section 1.6.2, Prentice Hall, 1997):

$$\log K_a = a + bT + \frac{c}{T} + d \log T + eT^2 \quad (2)$$

The parameters in this equation may be obtained by calibration in the laboratory over the desired temperature range using standard buffers of known pH. Dependence on pressure may also be obtained through experimental calibration if necessary. Several models have been proposed for activity coefficient estimation. For example, the Debye-Huckel equation is commonly used for low ionic strength solutions and the Pitzer model at higher ionic strengths (D. Langmuir, *Aqueous Environmental Geochemistry*, Chapter 4, Section 4.2, Prentice Hall, 1997). Ionic strengths can be derived from downhole water sample conductivity/resistivity measurements as is done in the MDT or alternatively from other wireline measurements such as resistivity logs. For very dilute solutions and/or for acid and base forms that have similar behaviours, the activity coefficient term may be neglected. Thus equation (1) provides a means for determining pH under downhole conditions for most

temperatures, pressures and ionic strengths encountered in practice.

As an example, Figure 2a shows the room temperature absorbance spectra of (a) the acid form of phenol red and (b) the base form of phenol red. The acid form has a peak at about 432 nm and the base form at about 559 nm. Figure 2a also shows (c) the measured absorbance spectrum of phenol red in a pH 8 solution, and (d) a weighted sum of the acid and base form spectra fitted to the measured absorbance spectrum, the weightings providing the base and acid fraction of phenol red in the pH 8 solution.

Similar analyses can be performed for solutions prepared with different pH levels. Figure 2b shows a graph of base fraction of phenol red (right hand vertical axis) as a function of prepared solution pH (horizontal axis). Using equation (1) it is then possible to calculate the pH of each solution. The calculated pH values (left hand vertical axis) are also plotted on Figure 2b. They show that, in this example, pH determined by spectroscopy is highly accurate for phenol red base fractions in the range of about 0.05 to 0.95 corresponding to pH values from 6.5 to 9. The range of pH measurement can be increased to 6 to 9.5 if the acid and base fractions can be spectroscopically detected at lower levels of 0.02.

The accuracy of the pH measurement is higher when the pH is close to the pKa value and decreases when the pH departs from the pKa. Thus, if the likely pH range is known, an indicator can be selected which has a pKa value such that a desired level of accuracy can be achieved. A combination of indicators may be chosen to cover the pH range typically expected in formation waters. In this way, provided the

optical analyser has suitable wavelength windows to observe the colour changes, the pH can be obtained to within a value of a few tenths. Depending on how the indicators interact with each other, multiple injectors in series or parallel may be used for the different indicators or a single injector with a mixed indicator solution may be deployed.

The analysis may be performed using a stable and calibrated colorimeter/spectrophotometer. Alternatively, the absorbance spectra of the water sample in the flow line prior to indicator injection can yield the baseline. Yet another option is to use a reference solution to calibrate the colorimeter/spectrophotometer. The last two options provide a means of compensating for any possible inherent water colour.

Further improvements may be obtained if a series of buffer reference solutions are supplied, each differing in pH e.g. by about 0.2 and covering the range around the expected pH value. Indicator is then added to known volumes of the buffer solution and the water sample and the colours compared to determine the pH. To ensure accuracy, preferably the water sample is a captured sample.

For downhole use, the indicator should be stable and chemically active at the temperatures expected downhole. As an example, Figure 3a shows the room temperature absorbance spectra obtained from (a) phenol red in deionised water and (b) phenol red in deionised water after heat treatment at 150°C for 24 hours. The heat treatment results in only a 10% loss in absorbance, demonstrating that the phenol red indicator can survive prolonged exposure to temperatures of up to 150°C.

However, it may be necessary to calibrate each indicator/reagent for the different temperatures and ionic

strengths to which it will be exposed downhole. Figure 3b shows the spectra obtained from (a) phenol red in a 7.4 pH buffer solution at 22°C and (b) phenol red in the 7.4 pH buffer solution at 150°C. At 150°C the phenol red is still
5 chemically active, the increase in base fraction at the higher temperature being due to changes in pKa and the pH of the buffer solution with temperature.

While the invention has been described in conjunction with the exemplary embodiments described above, many equivalent
10 modifications and variations will be apparent to those skilled in the art when given this disclosure. Accordingly, the exemplary embodiments of the invention set forth above are considered to be illustrative and not limiting. Various
15 changes to the described embodiments may be made without departing from the spirit and scope of the invention.

Claims

1. An apparatus for analysing water chemistry, the apparatus being adapted to operate downhole and comprising:

5 a colouring agent supply device for supplying a colouring agent to a water sample, the colour of the water sample thus supplied being indicative of the water sample chemistry, and
a colorimetric analyser arranged to determine the colour of the water sample.

10 2. An apparatus according to claim 1 which is installed downhole.

3. An apparatus according to claim 1 or 2 wherein the colorimetric analyser is operably connected to a processor which determines the water sample chemistry from the colour of the water sample.

15 4. An apparatus according to any one of the previous claims wherein the colorimetric analyser comprises a spectrometer

5. Use of the apparatus of any one of the previous claims for *in situ* analysis of downhole water chemistry.

20 6. A method for analysing downhole water chemistry, the method comprising the steps of:

(a) supplying a colouring agent to a downhole water sample, the colour of the water sample thus supplied being indicative of the water sample chemistry, and

25 (b) determining the colour of the water sample, wherein steps (a) and (b) are performed *in situ*.

7. A method for monitoring contamination of downhole water, the method comprising the steps of:

(a) adding a tracer agent to a fluid which is a potential contaminant of the downhole water,

(b) supplying a colouring agent to a sample of the downhole water, the colour of the water sample thus supplied being indicative of the presence of the tracer agent, and

(c) determining the colour of the water sample,

5 wherein steps (b) and (c) are performed *in situ*.

8. An apparatus for analysing water chemistry as herein described with reference to and as shown in the accompanying drawings.

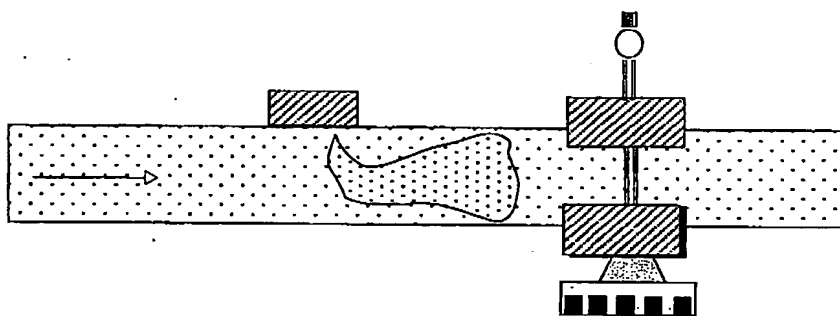


Fig. 1

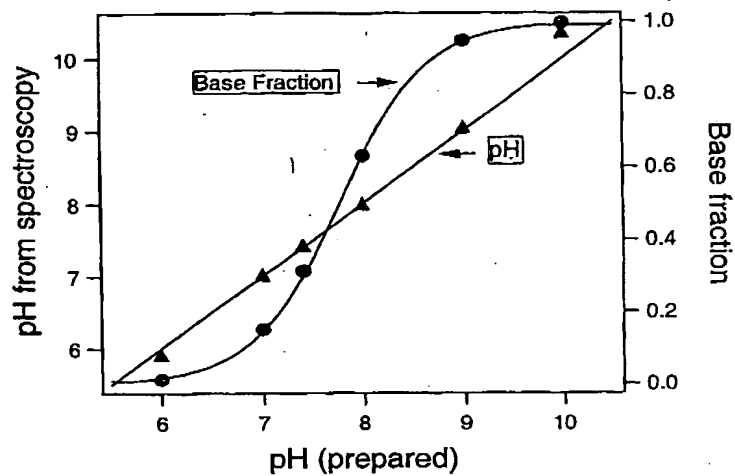
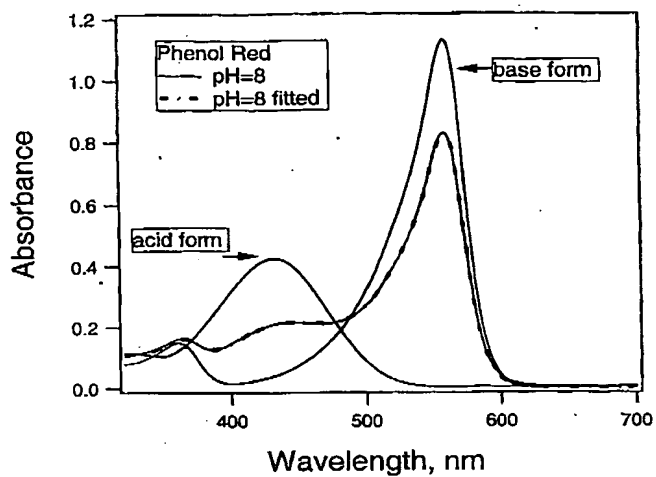


Fig. 2

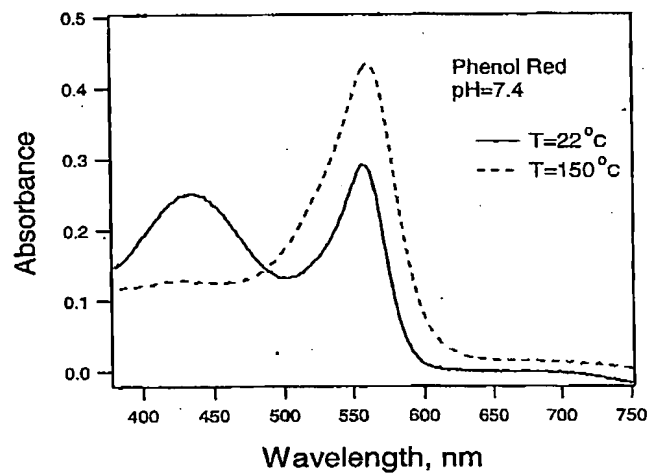
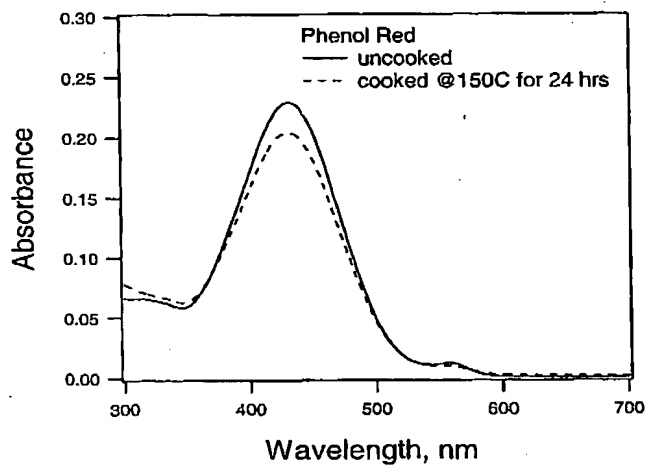


Fig. 3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 03/05016

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 G01N33/28 E21B49/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 G01N E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 476 384 B1 (OKUDA IKKO ET AL) 5 November 2002 (2002-11-05) column 10, line 5 - line 43 column 6, line 23 - line 54; figure 12 claims 18,20,22	1-7
X	US 2002/108910 A1 (LYON IRVING) 15 August 2002 (2002-08-15) paragraphs '0051!-'0053!,'0057!,'0065!-'0067!; figure 1	1-7
X	US 6 268 911 B1 (TUBEL PAULO ET AL) 31 July 2001 (2001-07-31) column 12, line 8 -column 15, line 49; figures 5-8	1-7
	-/-	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

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- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

1 April 2004

Date of mailing of the international search report

13/04/2004

Name and mailing address of the ISA

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Consalvo, D

INTERNATIONAL SEARCH REPORT

Application No

PCT/GB 03/05016

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 343 507 B1 (BUTSCH ROBERT J ET AL) 5 February 2002 (2002-02-05) column 6, line 44 -column 9, line 16; figures 6,7	1-7
A	MORRIS C W ET AL: "Using optical fluid analysis to evaluate downhole fluid sample contamination" SPE SOCIETY OF PETROLEUM ENGINEERS INC., no. 50603, 20 October 1998 (1998-10-20), pages 283-295, XP002251115 page 284, column 2, line 22 -page 285, column 1, line 33; figure 1	1-7
A	US 5 128 882 A (COOPER STAFFORD S ET AL) 7 July 1992 (1992-07-07) column 4, line 14 - line 59	1-7
P,A	AMMANN A A ET AL: "Ground water pollution by roof runoff infiltration evidenced with multi-tracer experiments" WATER RESEARCH, ELSEVIER SCIENCE PUBLISHERS, AMSTERDAM, NL, vol. 37, no. 5, March 2003 (2003-03), pages 1143-1153, XP004404138 ISSN: 0043-1354 paragraph '0005!	1-7

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 8

Claim 8 does not fulfil the requirements of Rule 6.2a) PCT.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/GB 03/05016

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 8
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

ional Application No

PCT/GB 03/05016

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
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